

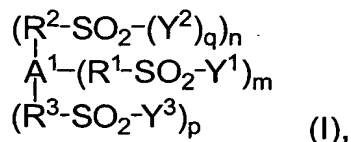
CLAIMS

What is claimed is:

AP20 Rec'd PCT/PTO 13 DEC 2005

1. A compound having the general structure:

5



10 wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings

R^1 , R^2 , and R^3 are divalent fluorinated groups;

m , n , and p are 0 to 3, with the proviso that $m + n + p$ is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

15 q is 0 or 1;

Y^1 is $-OH$, $-NH-SO_2-R^4$ wherein R^4 is a monovalent fluorinated group, $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, or

$-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein A^2 is a divalent heterocyclic group and R^5 , R^6 , and R^7 are divalent fluorinated groups; and

20 Y^2 and Y^3 are $-OH$ or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

25 2. The compound of claim 1 wherein the compound is a small molecule.

3. The compound of claim 1 wherein the compound is a repeat unit for a polymer.

4. The compound of claim 1, 2 or 3 wherein A^1 selected from the group consisting of oxadiazole, triazole, thiadiazole, pyrazole, triazine, 30 tetrazole, oxazole, thiazole, imidazole, benzoxazole, benzothiazole, benzimidazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.

5. The compound of claim 4 wherein A^1 is selected from the group consisting of [1,3,4]oxadiazole, [1,3,4]thiadiazole, and [1,2,4]triazole.

35 6. The compound of claim 5 wherein A^1 is [1,3,4]oxadiazole.

7. The compound of claim 1, 2, or 3 wherein R^1 , R^2 , and R^3 are linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.
8. The compound of claim 7 wherein R^1 , R^2 , and R^3 are linear or branched perfluorinated saturated or unsaturated groups having 1 to 10 carbon atoms optionally containing ethereal oxygen atoms.
9. The compound of claim 8 wherein R^1 , R^2 , and R^3 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.
10. The compound of claim 1, 2, or 3 wherein $m + n + p$ is equal to 2 or 3.
11. The compound of claim 10 wherein $m + n + p$ is equal to 2.
12. The compound of claim 1 or 3 wherein A^2 is a divalent aromatic heterocyclic group, such as an oxadiazole, triazole, thiadiazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.
13. The compound of claim 12 wherein A^2 is [1,3,4]oxadiazole.
14. The compound of claim 1 or 3 wherein R^5 , R^6 , and R^7 are linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.
15. The compound of claim 1 or 2 wherein Y^1 , Y^2 , and Y^3 are each equal to $-OH$ or $-NH-SO_2-R^4$, wherein R^4 is any monovalent fluorinated group, and q is 1.
16. The compound of claim 15 wherein R^4 is a linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated group having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.
17. The compound of claim 15 wherein $m + n + p$ is equal to 2 or 3.
18. The compound of claim 1 or 2 wherein Y^1 is $-NH-SO_2-R^4$, n and p are each equal to 0, and m is 2 or 3.
19. The compound of claim 1 or 3 wherein m and n is each equal to 1, p is 0 to 1, and q is 0.

20. The compound of claim 19 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-$.

21. The compound of claim 19 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^5-SO_2-NH-$, wherein R^5 is a divalent fluorinated group.

22. The compound of claim 19 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein R^6 and R^7 are a divalent fluorinated groups.

23. A compound of claim 1 or 3 wherein the compound is a random copolymer obtained by randomly combining any variety of the polymer repeat units, in any ratio with respect to each other, wherein m and n are each equal to 1, p is 0 to 1 and q is 0.

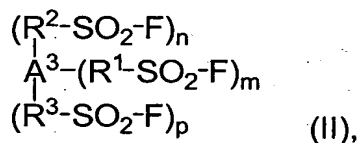
24. A compound of claim 1 or 2 wherein A^1 is a divalent aromatic heterocyclic group, m is 2, n and p are each equal to 0, and Y^1 is $-NH-SO_2-R^4$.

25. A compound of claim 1 or 3 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-$.

26. A compound of claim 1 or 3 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^5-SO_2-NH-$.

27. A compound of claim 1 or 3 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

28. A fluorinated fluorosulfonyl-substituted heterocycle having the general structure:



wherein A^3 is a divalent or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1 , R^2 , and R^3 are divalent fluorinated groups;

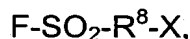
5 m , n , and p are 0 to 3, with the proviso that $m + n + p$ is equal to 2 or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by fluorinated fluorosulfonyl groups.

29. The fluorinated fluorosulfonyl-substituted heterocycle of claim
10 28 wherein A^3 is a divalent aromatic heterocyclic group, m and n are each equal to 1, and p is 0.

30. The fluorinated fluorosulfonyl-substituted heterocycle of claim
28 wherein A^3 is a divalent aromatic heterocyclic group, n and p are each equal to 0, and m is 2.

15 31. A process for synthesizing a compound comprising the following steps:

(a) providing a fluorosulfonyl-containing acyl derivative having the structure:



20 wherein R^8 is a divalent fluorinated group as defined above for R^1 and X is an acyl group;

(b) condensing the fluorosulfonyl-containing acyl derivative from step (a) with a nitrogenous reagent to form a sulfonyl-containing precursor;

(c) cyclizing the sulfonyl-containing precursor of step (b) by
25 thermolysis or dehydration to form a sulfonyl-containing aromatic heterocyclic compound containing fluorosulfonyl groups or sulfonamide groups; and

(d) converting the sulfonyl-containing aromatic heterocyclic compound of step (c) containing fluorosulfonyl groups or sulfonamide
30 groups, into an acidic sulfonyl-containing aromatic heterocyclic compound by either:

(i) condensing fluorosulfonyl groups with a fluorinated sulfonamide,
(ii) condensing sulfonamide groups with a fluorinated sulfonyl fluoride,

35 (iii) condensing fluorosulfonyl groups first with ammonia to form sulfonamide groups followed by a fluorinated sulfonyl fluoride to

form sulfonimide groups, or

(iv) hydrolysis of fluorosulfonyl or sulfonamide groups to form sulfonic acid groups.

32. The process of claim 31 wherein the acyl group is selected from the group consisting of acyl fluoride, acyl chloride, acyl bromide, acyl iodide, an ester, an amide, and nitrile.

33. The process of claim 31 wherein the nitrogenous reagent, is selected from the group consisting of ammonia; hydrazine; an azide; and an organic ortho-substituted aromatic amine.

34. A process for synthesizing a bis(sulfonimide)-[1,3,4]oxadiazole by condensing a fluorosulfonyl acyl fluoride, $F-SO_2-R^8-CO-F$, with hydrazine to form a bis(fluorosulfonyl)dihydrazide containing a dihydrazide group and fluorosulfonyl groups; forming a [1,3,4]oxadiazole ring by cyclizing the dihydrazide group using dehydration; condensing the fluorosulfonyl groups with ammonia to form a bis(sulfonamide)-[1,3,4]oxadiazole containing sulfonamide groups; and forming sulfonimide groups by condensing a fluorinated sulfonyl fluoride, R^4-SO_2-F , with the sulfonamide groups, wherein R^4 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

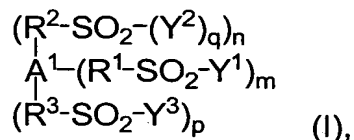
35. A process for synthesizing a copolymer containing sulfonimide and [1,3,4]oxadiazole groups by condensing a fluorosulfonyl acyl fluoride, $F-SO_2-R^8-CO-F$, with hydrazine to form a bis(fluorosulfonyl)dihydrazide containing a dihydrazide group and fluorosulfonyl groups; forming a [1,3,4]oxadiazole ring by cyclizing the dihydrazide group using dehydration; condensing the fluorosulfonyl groups with ammonia to form a bis(sulfonamide)-[1,3,4]oxadiazole containing sulfonamide groups; and forming sulfonimide groups by condensing a fluorinated disulfonyl difluoride, $F-SO_2-R^5-SO_2-F$, with the sulfonamide groups, wherein R^5 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

36. A process for synthesizing a benzimidazole sulfonimide by condensing a fluorosulfonyl acyl fluoride, $F-SO_2-R^8-CO-F$, with ammonia to form a diamide containing a carbamide group and a sulfonamide group; condensing the carbamide group with an ortho-phenylene diamine to form a carbamide adduct; cyclizing the carbamide adduct by thermolysis to form a benzimidazole group, and forming a sulfonimide group by condensing a fluorinated sulfonyl fluoride, R^4-SO_2-F , with the sulfonamide group,

wherein R^4 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

37. A process for synthesizing a benzimidazole sulfonic acid by condensing a fluorosulfonyl acyl fluoride, $F-SO_2-R^8-CO-F$, with an ortho-phenylene diamine to form a carbamide adduct; cyclizing the carbamide adduct by thermolysis to form a benzimidazole group, and forming a sulfonic acid group by hydrolyzing the fluorosulfonyl group wherein R^8 is a linear perfluorinated saturated group having 1 to 6 carbon atoms.

38. A solid polymer electrolyte membrane comprising a porous substrate having imbibed therein a compound having the general structure:



wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1 , R^2 , and R^3 are divalent fluorinated groups;

m , n , and p are 0 to 3, with the proviso that $m + n + p$ is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

Y^1 is $-OH$, $-NH-SO_2-R^4$ wherein R^4 is a monovalent fluorinated group, $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, or

$-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein A^2 is a divalent aromatic heterocyclic group and R^5 , R^6 , and R^7 are divalent fluorinated groups; and

Y^2 and Y^3 are $-OH$ or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

39. The solid polymer electrolyte membrane of claim 38 wherein the porous substrate is selected from the group consisting of inorganic fiber substrates and microporous films of perfluorinated polymers.

40. The solid polymer electrolyte membrane of claim 38 wherein the compound is a small molecule.

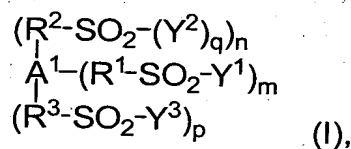
41. The solid polymer electrolyte membrane of claim 38 wherein the compound is a repeat unit for a polymer.

42. The solid polymer electrolyte membrane of claim 38 wherein the compound is cross linked, grafted, or chain extended within the porous support.

43. The solid polymer electrolyte membrane of claim 42 wherein the compound is modified to contain reactive functional groups to provide crosslinking, grafting, or chain extension.

44. The solid polymer electrolyte membrane of claim 42 wherein the compound is mixed with reagents to provide crosslinking, grafting, or chain extension.

45. A catalyst coated membrane comprising a solid polymer electrolyte membrane having a first surface and a second surface, an anode present on the first surface of the solid polymer electrolyte membrane, and a cathode present on the second surface of the solid polymer electrolyte membrane, wherein the solid polymer electrolyte membrane comprises a porous substrate having imbibed therein a compound having the general structure:



wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1 , R^2 , and R^3 are divalent fluorinated groups;

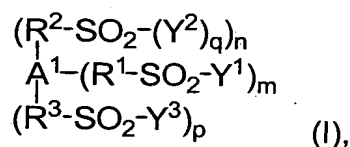
m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

5 Y¹ is -OH, -NH-SO₂-R⁴ wherein R⁴ is a monovalent fluorinated group, -NH-, -NH-SO₂-R⁵-SO₂-NH-, or -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-, wherein A² is a divalent aromatic heterocyclic group and R⁵, R⁶, and R⁷ are divalent fluorinated groups; and

10 Y² and Y³ are -OH or -NH-SO₂-R⁴; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y¹ is selected from the group consisting of -NH-, -NH-SO₂-R⁵-SO₂-NH-, and -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-.

15 46. A membrane electrode assembly comprising a polymer electrolyte membrane having a first surface and a second surface, and comprising a compound having the general structure:



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wherein A¹ is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R¹, R², and R³ are divalent fluorinated groups;

25 m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

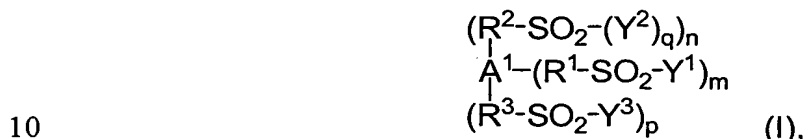
q is 0 or 1;

30 Y¹ is -OH, -NH-SO₂-R⁴ wherein R⁴ is a monovalent fluorinated group, -NH-, -NH-SO₂-R⁵-SO₂-NH-, or -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-, wherein A² is a divalent aromatic heterocyclic group and R⁵, R⁶, and R⁷ are divalent fluorinated groups; and

Y^2 and Y^3 are $-OH$ or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

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47. An electrocatalyst coating composition comprising a compound having the general structure:



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wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

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R^1 , R^2 , and R^3 are divalent fluorinated groups;

m , n , and p are 0 to 3, with the proviso that $m + n + p$ is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

20

Y^1 is $-OH$, $-NH-SO_2-R^4$ wherein R^4 is a monovalent fluorinated group, $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, or

$-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein A^2 is a divalent aromatic heterocyclic group and R^5 , R^6 , and R^7 are divalent fluorinated groups; and

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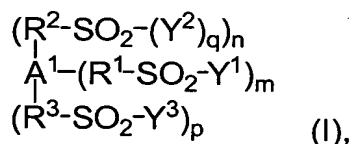
Y^2 and Y^3 are $-OH$ or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

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48. An electrocatalyst coating composition of claim 47 further

comprising a catalyst.

49. An electrochemical cell comprising a polymer electrolyte membrane, wherein the polymer electrolyte membrane comprises a compound having the general structure:



5 wherein A¹ is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R¹, R², and R³ are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

Y¹ is -OH, -NH-SO₂-R⁴ wherein R⁴ is a monovalent fluorinated group, -NH-, -NH-SO₂-R⁵-SO₂-NH-, or

-NH-SO₂-R⁶-A²-R⁷-SO₂-NH-, wherein A² is a divalent aromatic heterocyclic group and R⁵, R⁶, and R⁷ are divalent fluorinated groups; and

Y² and Y³ are -OH or -NH-SO₂-R⁴; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y¹ is selected from the group consisting of -NH-, -NH-SO₂-R⁵-SO₂-NH-, and -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-.

50. The electrochemical cell of claim 49 selected from the group consisting of fuel cells, batteries, chloralkali cells, electrolysis cells, sensors, electrochemical capacitors, and modified electrodes.

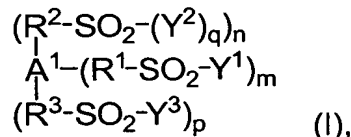
CLAIMS

AP20 Rec'd PCT/PTO 13 DEC 2005

What is claimed is:

1. A compound having the general structure:

5



10 wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings

R^1 , R^2 , and R^3 are divalent fluorinated groups;

m , n , and p are 0 to 3, with the proviso that $m + n + p$ is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

15 q is 0 or 1;

Y^1 is $-OH$, $-NH-SO_2-R^4$ wherein R^4 is a monovalent fluorinated group, $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, or

$-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein A^2 is a divalent heterocyclic group and R^5 , R^6 , and R^7 are divalent fluorinated groups; and

20 Y^2 and Y^3 are $-OH$ or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

25 2. The compound of claim 1 wherein the compound is a small molecule.

3. The compound of claim 1 wherein the compound is a repeat unit for a polymer.

4. The compound of claim 1, 2 or 3 wherein A^1 selected from the group consisting of oxadiazole, triazole, thiadiazole, pyrazole, triazine, 30 tetrazole, oxazole, thiazole, imidazole, benzoxazole, benzothiazole, benzimidazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.

5. The compound of claim 4 wherein A^1 is selected from the group consisting of [1,3,4]oxadiazole, [1,3,4]thiadiazole, and [1,2,4]triazole.

35 6. The compound of claim 5 wherein A^1 is [1,3,4]oxadiazole.

7. The compound of claim 1, 2, or 3 wherein R^1 , R^2 , and R^3 are linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing
5 etheral oxygen, chlorine, bromine, or iodine atoms.
8. The compound of claim 7 wherein R^1 , R^2 , and R^3 are linear or branched perfluorinated saturated or unsaturated groups having 1 to 10 carbon atoms optionally containing etheral oxygen atoms.
9. The compound of claim 8 wherein R^1 , R^2 , and R^3 are linear
10 perfluorinated saturated groups having 1 to 6 carbon atoms.
10. The compound of claim 1, 2, or 3 wherein $m + n + p$ is equal to 2 or 3.
11. The compound of claim 10 wherein $m + n + p$ is equal to 2.
12. The compound of claim 1 or 3 wherein A^2 is a divalent aromatic
15 heterocyclic group, such as an oxadiazole, triazole, thiadiazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.
13. The compound of claim 12 wherein A^2 is [1,3,4]oxadiazole.
14. The compound of claim 1 or 3 wherein R^5 , R^6 , and R^7 are
20 linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing etheral oxygen, chlorine, bromine, or iodine atoms.
15. The compound of claim 1 or 2 wherein Y^1 , Y^2 , and Y^3 are each equal to $-OH$ or $-NH-SO_2-R^4$, wherein R^4 is any monovalent fluorinated
25 group, and q is 1.
16. The compound of claim 15 wherein R^4 is a linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated group having 1 to 20 carbon atoms optionally containing etheral oxygen, chlorine, bromine, or iodine atoms.
17. The compound of claim 15 wherein $m + n + p$ is equal to 2 or 3.
18. The compound of claim 1 or 2 wherein Y^1 is $-NH-SO_2-R^4$, n
30 and p are each equal to 0, and m is 2 or 3.
19. The compound of claim 1 or 3 wherein m and n is each equal to 1, p is 0 to 1, and q is 0.
20. The compound of claim 19 wherein A^1 is a divalent aromatic
35 heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-$.

21. The compound of claim 19 wherein A¹ is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y¹ is -NH-SO₂-R⁵-SO₂-NH-, wherein R⁵ is a divalent fluorinated group.

22. The compound of claim 19 wherein A¹ is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y¹ is -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-, wherein R⁶ and R⁷ are a divalent fluorinated groups.

23. A compound of claim 1 or 3 wherein the compound is a random copolymer obtained by randomly combining any variety of the polymer repeat units, in any ratio with respect to each other, wherein m and n are each equal to 1, p is 0 to 1 and q is 0.

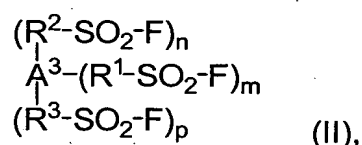
24. A compound of claim 1 or 2 wherein A¹ is a divalent aromatic heterocyclic group, m is 2, n and p are each equal to 0, and Y¹ is -NH-SO₂-R⁴.

25. A compound of claim 1 or 3 wherein A¹ is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y¹ is -NH-.

26. A compound of claim 1 or 3 wherein A¹ is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y¹ is -NH-SO₂-R⁵-SO₂-NH-.

27. A compound of claim 1 or 3 wherein A¹ is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y¹ is -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-.

28. A fluorinated fluorosulfonyl-substituted heterocycle having the general structure:



wherein A³ is a divalent or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R¹, R², and R³ are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 2

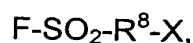
or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by fluorinated fluorosulfonyl groups.

29. The fluorinated fluorosulfonyl-substituted heterocycle of claim 28 wherein A³ is a divalent aromatic heterocyclic group, m and n are each equal to 1, and p is 0.

5 30. The fluorinated fluorosulfonyl-substituted heterocycle of claim 28 wherein A³ is a divalent aromatic heterocyclic group, n and p are each equal to 0, and m is 2.

31. A process for synthesizing a compound comprising the following steps:

10 (a) providing a fluorosulfonyl-containing acyl derivative having the structure:



wherein R⁸ is a divalent fluorinated group as defined above for R¹ and X is an acyl group;

15 (b) condensing the fluorosulfonyl-containing acyl derivative from step (a) with a nitrogenous reagent to form a sulfonyl-containing precursor;

 (c) cyclizing the sulfonyl-containing precursor of step (b) by thermolysis or dehydration to form a sulfonyl-containing aromatic heterocyclic compound containing fluorosulfonyl groups or sulfonamide groups; and

20 (d) converting the sulfonyl-containing aromatic heterocyclic compound of step (c) containing fluorosulfonyl groups or sulfonamide groups, into an acidic sulfonyl-containing aromatic heterocyclic compound by either:

25 (i) condensing fluorosulfonyl groups with a fluorinated sulfonamide, (ii) condensing sulfonamide groups with a fluorinated sulfonyl fluoride,

 (iii) condensing fluorosulfonyl groups first with ammonia to form sulfonamide groups followed by a fluorinated sulfonyl fluoride to form sulfonimide groups, or

30 (iv) hydrolysis of fluorosulfonyl or sulfonamide groups to form sulfonic acid groups.

32. The process of claim 31 wherein the acyl group is selected from the group consisting of acyl fluoride, acyl chloride, acyl bromide, acyl iodide, an ester, an amide, and nitrile.

35 33. The process of claim 31 wherein the nitrogenous reagent, is selected from the group consisting of ammonia; hydrazine; an azide; and an organic ortho-substituted aromatic amine.

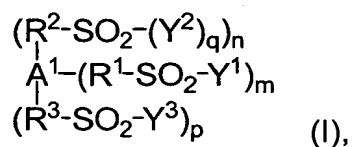
34. A process for synthesizing a bis(sulfonimide)-[1,3,4]oxadiazole by condensing a fluorosulfonyl acyl fluoride, $F-SO_2-R^8-CO-F$, with hydrazine to form a bis(fluorosulfonyl)dihydrazide containing a dihydrazide group and fluorosulfonyl groups; forming a [1,3,4]oxadiazole ring by cyclizing the dihydrazide group using dehydration; condensing the fluorosulfonyl groups with ammonia to form a bis(sulfonamide)-[1,3,4]oxadiazole containing sulfonamide groups; and forming sulfonimide groups by condensing a fluorinated sulfonyl fluoride, R^4-SO_2-F , with the sulfonamide groups, wherein R^4 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

35. A process for synthesizing a copolymer containing sulfonimide and [1,3,4]oxadiazole groups by condensing a fluorosulfonyl acyl fluoride, $F-SO_2-R^8-CO-F$, with hydrazine to form a bis(fluorosulfonyl)dihydrazide containing a dihydrazide group and fluorosulfonyl groups; forming a [1,3,4]oxadiazole ring by cyclizing the dihydrazide group using dehydration; condensing the fluorosulfonyl groups with ammonia to form a bis(sulfonamide)-[1,3,4]oxadiazole containing sulfonamide groups; and forming sulfonimide groups by condensing a fluorinated disulfonyl difluoride, $F-SO_2-R^5-SO_2-F$, with the sulfonamide groups, wherein R^5 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

36. A process for synthesizing a benzimidazole sulfonimide by condensing a fluorosulfonyl acyl fluoride, $F-SO_2-R^8-CO-F$, with ammonia to form a diamide containing a carbamide group and a sulfonamide group; condensing the carbamide group with an ortho-phenylene diamine to form a carbamide adduct; cyclizing the carbamide adduct by thermolysis to form a benzimidazole group, and forming a sulfonimide group by condensing a fluorinated sulfonyl fluoride, R^4-SO_2-F , with the sulfonamide group, wherein R^4 and R^8 are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

37. A process for synthesizing a benzimidazole sulfonic acid by condensing a fluorosulfonyl acyl fluoride, $F-SO_2-R^8-CO-F$, with an ortho-phenylene diamine to form a carbamide adduct; cyclizing the carbamide adduct by thermolysis to form a benzimidazole group, and forming a sulfonic acid group by hydrolyzing the fluorosulfonyl group wherein R^8 is a linear perfluorinated saturated group having 1 to 6 carbon atoms.

38. A solid polymer electrolyte membrane comprising a porous substrate having imbibed therein a compound having the general structure:



5

wherein A¹ is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R¹, R², and R³ are divalent fluorinated groups;

10 m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

Y¹ is -OH, -NH-SO₂-R⁴ wherein R⁴ is a monovalent fluorinated group, -NH-, -NH-SO₂-R⁵-SO₂-NH-, or

15 -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-, wherein A² is a divalent aromatic heterocyclic group and R⁵, R⁶, and R⁷ are divalent fluorinated groups; and

20 Y² and Y³ are -OH or -NH-SO₂-R⁴; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y¹ is selected from the group consisting of -NH-, -NH-SO₂-R⁵-SO₂-NH-, and -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-.

39. The solid polymer electrolyte membrane of claim 38 wherein the porous substrate is selected from the group consisting of inorganic fiber substrates and microporous films of perfluorinated polymers.

25 40. The solid polymer electrolyte membrane of claim 38 wherein the compound is a small molecule.

41. The solid polymer electrolyte membrane of claim 38 wherein the compound is a repeat unit for a polymer.

30 42. The solid polymer electrolyte membrane of claim 38 wherein the compound is cross linked, grafted, or chain extended within the porous support.

43. The solid polymer electrolyte membrane of claim 42 wherein the compound is modified to contain reactive functional groups to provide crosslinking, grafting, or chain extension.

44. The solid polymer electrolyte membrane of claim 42 wherein the compound is mixed with reagents to provide crosslinking, grafting, or chain extension.

5 ~~45. The solid polymer electrolyte membrane of claim 38, 40 or 41 wherein A¹ selected from the group consisting of oxadiazole, triazole, thiadiazole, pyrazole, triazine, tetrazole, oxazole, thiazole, imidazole, benzoxazole, benzothiazole, benzimidazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.~~

10 ~~46. The solid polymer electrolyte membrane of claim 45 wherein A¹ is selected from the group consisting of [1,3,4]oxadiazole, [1,3,4]thiadiazole and [1,2,4]triazole.~~

~~47. The solid polymer electrolyte membrane of claim 46 wherein A¹ is [1,3,4]oxadiazole.~~

15 ~~48. The solid polymer electrolyte membrane of claim 38, 40, or 41 wherein R¹, R², and R³ are linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.~~

20 ~~49. The solid polymer electrolyte membrane of claim 48 wherein R¹, R², and R³ are linear or branched perfluorinated saturated or unsaturated groups having 1 to 10 carbon atoms optionally containing ethereal oxygen atoms.~~

25 ~~50. The solid polymer electrolyte membrane of claim 49 wherein R¹, R², and R³ are linear perfluorinated saturated groups having 1 to 6 carbon atoms.~~

~~51. The solid polymer electrolyte membrane of claim 38, 40, or 41 wherein m + n + p is equal to 2 or 3.~~

30 ~~52. The solid polymer electrolyte membrane of claim 51 wherein m + n + p is equal to 2.~~

~~53. The solid polymer electrolyte membrane of claim 38 or 41 wherein A² is a divalent aromatic heterocyclic group, such as an oxadiazole, triazole, thiadiazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.~~

35 ~~54. The solid polymer electrolyte membrane of claim 53 wherein A² is [1,3,4]oxadiazole.~~

~~55. The solid polymer electrolyte membrane of claim 38 or 41 wherein R⁵, R⁶, and R⁷ are linear, branched, or cyclic perfluorinated or~~

~~partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.~~

56. ~~The solid polymer electrolyte membrane of claim 38 or 40 wherein Y^1 , Y^2 , and Y^3 are each equal to $-OH$ or $-NH-SO_2-R^4$, wherein R^4 is any monovalent fluorinated group, and q is 1.~~

57. ~~The solid polymer electrolyte membrane of claim 56 wherein R^4 is a linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated group having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.~~

58. ~~The solid polymer electrolyte membrane of claim 56 wherein $m + n + p$ is equal to 2 or 3.~~

59. ~~The solid polymer electrolyte membrane of claim 38 or 40 wherein Y^1 is $-NH-SO_2-R^4$, n and p are each equal to 0 and m is 2 or 3.~~

60. ~~The solid polymer electrolyte membrane of claim 38 or 41 wherein m and n is each equal to 1, p is 0 to 1, and q is 0.~~

61. ~~The solid polymer electrolyte membrane of claim 60 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-$.~~

62. ~~The solid polymer electrolyte membrane of claim 60 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^5-SO_2-NH-$, wherein R^5 is a divalent fluorinated group.~~

63. ~~The solid polymer electrolyte membrane of claim 60 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein R^6 and R^7 are a divalent fluorinated groups.~~

64. ~~The solid polymer electrolyte membrane of claim 38 or 41 wherein the compound is a random copolymer obtained by randomly combining any variety of the polymer repeat units, in any ratio with respect to each other, wherein m and n are each equal to 1, p is 0 to 1 and q is 0.~~

65. ~~The solid polymer electrolyte membrane of claim 38 or 40 wherein A^1 is a divalent aromatic heterocyclic group, m is 2, n and p are each equal to 0, and Y^1 is $-NH-SO_2-R^4$.~~

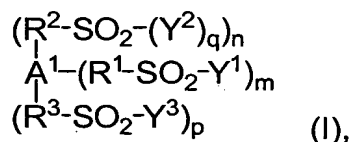
66. ~~The solid polymer electrolyte membrane of claim 38 or 41 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-$.~~

67. The solid polymer electrolyte membrane of claim 38 or 41 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^5-SO_2-NH-$.

5 68. The solid polymer electrolyte membrane of claim 38 or 41 wherein A^1 is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y^1 is $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

6945. A catalyst coated membrane comprising a solid polymer electrolyte membrane having a first surface and a second surface, an anode present on the first surface of the solid polymer electrolyte
10 membrane, and a cathode present on the second surface of the solid polymer electrolyte membrane, wherein the solid polymer electrolyte membrane comprises a porous substrate having imbibed therein a compound having the general structure:

15



20 wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1 , R^2 , and R^3 are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that $m + n + p$ is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

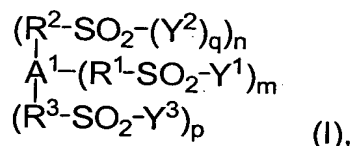
25 q is 0 or 1;

Y^1 is $-OH$, $-NH-SO_2-R^4$ wherein R^4 is a monovalent fluorinated group, $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, or

$-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein A^2 is a divalent aromatic heterocyclic group and R^5 , R^6 , and R^7 are divalent fluorinated
30 groups; and

Y^2 and Y^3 are $-OH$ or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

7046. A membrane electrode assembly comprising a polymer electrolyte membrane having a first surface and a second surface, and comprising a compound having the general structure:



wherein A¹ is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R¹, R², and R³ are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

Y¹ is -OH, -NH-SO₂-R⁴ wherein R⁴ is a monovalent fluorinated group, -NH-, -NH-SO₂-R⁵-SO₂-NH-, or

-NH-SO₂-R⁶-A²-R⁷-SO₂-NH-, wherein A² is a divalent aromatic heterocyclic group and R⁵, R⁶, and R⁷ are divalent fluorinated groups; and

Y² and Y³ are -OH or -NH-SO₂-R⁴; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y¹ is selected from the group consisting of -NH-, -NH-SO₂-R⁵-SO₂-NH-, and -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-.

~~71. The membrane electrode assembly of claim 70 wherein the solid polymer electrolyte further comprises a porous support.~~

~~72. The membrane electrode assembly of claim 70 further comprising at least one electrode prepared from an electrocatalyst coating composition present on the first and second surfaces of the polymer electrolyte membrane.~~

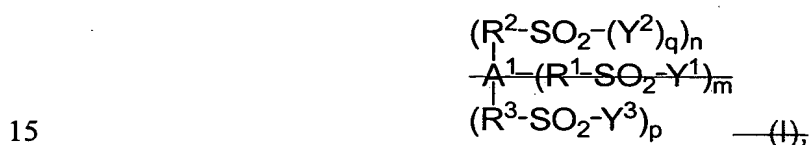
~~73. The membrane electrode assembly of claim 72 further comprising at least one gas diffusion backing present on at least one electrode, on the side away from the polymer electrolyte membrane.~~

74. ~~The membrane electrode assembly of claim 70 further comprising at least one gas diffusion electrode present on the first and second surfaces of the polymer electrolyte membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst coating composition.~~

75. ~~The membrane electrode assembly of claim 72 or 74 wherein the electrode is an anode.~~

76. ~~The membrane electrode assembly of claim 72 or 74 wherein the electrode is a cathode.~~

77. ~~The membrane electrode assembly of claim 72 or 74 wherein the electrocatalyst coating composition comprises a compound having the general structure:~~



wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R^1 , R^2 , and R^3 are divalent fluorinated groups;

m , n , and p are 0 to 3, with the proviso that $m + n + p$ is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

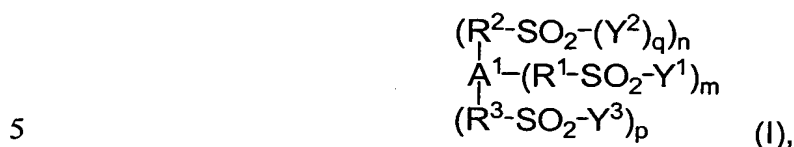
Y^1 is $-OH$, $-NH-SO_2-R^4$ wherein R^4 is a monovalent fluorinated group, $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, or

$-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein A^2 is a divalent aromatic heterocyclic group and R^5 , R^6 , and R^7 are divalent fluorinated groups; and

Y^2 and Y^3 are $-OH$ or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

78. ~~The membrane electrode assembly of claim 77 wherein the electrocatalyst coating composition further comprises a catalyst.~~

7947. An electrocatalyst coating composition comprising a compound having the general structure:

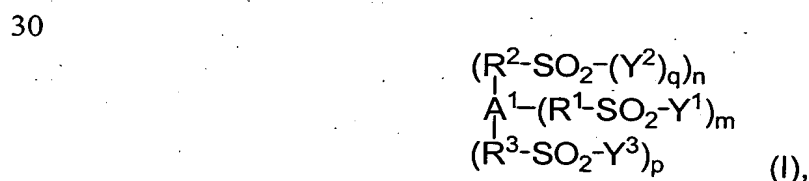


wherein A^1 is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

- 10 R^1 , R^2 , and R^3 are divalent fluorinated groups;
 m , n , and p are 0 to 3, with the proviso that $m + n + p$ is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;
 q is 0 or 1;
- 15 Y^1 is $-OH$, $-NH-SO_2-R^4$ wherein R^4 is a monovalent fluorinated group, $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, or $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$, wherein A^2 is a divalent aromatic heterocyclic group and R^5 , R^6 , and R^7 are divalent fluorinated groups; and
- 20 Y^2 and Y^3 are $-OH$ or $-NH-SO_2-R^4$; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y^1 is selected from the group consisting of $-NH-$, $-NH-SO_2-R^5-SO_2-NH-$, and $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$.

8048. An electrocatalyst coating composition of claim 7947 further comprising a catalyst.

8149. An electrochemical cell comprising a polymer electrolyte membrane, wherein the polymer electrolyte membrane comprises a compound having the general structure:



wherein A¹ is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R¹, R², and R³ are divalent fluorinated groups;

5 m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups;

q is 0 or 1;

10 Y¹ is -OH, -NH-SO₂-R⁴ wherein R⁴ is a monovalent fluorinated group, -NH-, -NH-SO₂-R⁵-SO₂-NH-, or -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-, wherein A² is a divalent aromatic heterocyclic group and R⁵, R⁶, and R⁷ are divalent fluorinated groups; and

15 Y² and Y³ are -OH or -NH-SO₂-R⁴; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y¹ is selected from the group consisting of -NH-, -NH-SO₂-R⁵-SO₂-NH-, and -NH-SO₂-R⁶-A²-R⁷-SO₂-NH-.

8250. The electrochemical cell of claim 84 49 selected from the group consisting of fuel cells, batteries, chloralkali cells, electrolysis cells, 20 sensors, electrochemical capacitors, and modified electrodes.

~~83. The electrochemical cell of claim 82, wherein the electrochemical cell is a fuel cell.~~

~~84. The fuel cell of claim 83 wherein the polymer electrolyte membrane further comprises a porous support.~~

25 ~~85. The fuel cell of claim 84 wherein the compound is imbibed into the porous support.~~

~~86. The fuel cell of claim 83 further comprising an anode and a cathode present on the first and second surfaces of the solid polymer electrolyte membrane.~~

30 ~~87. The fuel cell of claim 86 comprising at least one gas diffusion backing present on the side of the anode or cathode away from the solid polymer electrolyte membrane.~~

~~88. The fuel cell of claim 83 comprising gas diffusion electrodes, wherein the gas diffusion electrodes comprise at least one electrode on a gas diffusion backing, wherein the electrode is present in contact with the solid polymer electrolyte membrane.~~

35 ~~89. The fuel cell of claim 88 wherein the electrode is an anode.~~

~~90. The fuel cell of claim 88 wherein the electrode is a cathode.~~

91. ~~The fuel cell of claim 88 wherein the electrodes comprise an anode and a cathode.~~

5 92. ~~The fuel cell of claim 86 or 91 further comprising a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, a fuel in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode.~~

93. ~~The fuel cell of claim 83, 86 or 88 wherein the fuel is hydrogen.~~

10 94. ~~The fuel cell of claim 83, 86 or 88 wherein the fuel is an alcohol.~~

95. ~~The fuel cell of claim 94 wherein the fuel is methanol.~~